Introduction

Plutonium is often inaccurately identified in the media as the "most toxic substance known to man." Indeed, the element and its compounds are hazardous, and measures must be employed to protect workers, the public, and the environment. Minimizing the potential for release of plutonium is a primary concern at TA-55. Plutonium already in the environment, however, receives comparatively little attention.

An accurate assessment of the hazard posed by environmental plutonium is difficult, but substantial advances in this assessment are reported. Areas of investigation include determining the amount of environmental plutonium, describing its distribution and migration, and evaluating its biological and health consequences. These topics are of increasing interest as a result of the expanding use of plutonium in mixed oxide fuels for power generation in other countries. This article attempts to summarize important aspects of the subject for readers of the Actinide Research Quarterly.
Approximately 92% of environmental Pu is attributed to atmospheric testing.

Aboveground nuclear testing is estimated at 7400 tera (10^{12}) Becquerels (TBq—see box) and accounts for about 3.3 metric tons of plutonium. The total alpha activity resulting from $^{239}$Pu in the environment is about 1200 TBq, or about 2 kilograms of plutonium. Approximately 92% of environmental Pu is attributed to atmospheric testing.

Relatively small amounts of plutonium result from accidents. About 15 kilograms (90 TBq) of plutonium was released from the reactor at Chernobyl. The contribution from military sources is even smaller. For example, the aircraft accident involving nuclear weapons near Thule, Greenland, in 1968 released about 0.9 TBq of alpha activity from plutonium.

The rate of plutonium deposition in the environment has varied substantially over the past fifty years. The largest rates were during the period of atmospheric testing in the 1950s and early 1960s. Releases from reprocessing facilities reached a maximum estimated rate of 70 TBq per year during the mid 1970s, but are currently at about 0.1 TBq per year as a result of improved facilities and procedures. A major concern for reprocessing and storage facilities is the potential catastrophic loss of containment and a high, localized release of material.

Global distribution of plutonium is inhomogeneous. Concentrations are high at mid-latitude zones of each hemisphere and are highest in the northern hemisphere, where most atmospheric nuclear tests were conducted. Maximum $^{238}$Pu activities (70 Bq–80 Bq per square meter) appear at 35°–45° north latitude. Activities of the isotope are about 15 Bq per square meter at mid latitudes of the southern hemisphere and are 1 Bq–10 Bq per square meter near the equator and poles.

**Behavior of Environmental Plutonium**

Studies show that Pu exists primarily as an oxide in land deposits and in ocean sediments. Behavior in the environment is strongly dependent on the physical and chemical conditions of both the material and the medium. Important properties of the oxide are particle size and solubility. Plutonium appears in water as ionic species of Pu(IV) and Pu(VI).

When plutonium is released into the atmosphere, its behavior depends on the particle size and the dispersal mechanism. Stratospheric aerosols formed by nuclear testing and satellite burnup distribute globally over a period of years; material released by accidents typically deposit locally within minutes or hours. Airborne redistribution of potentially dispersible particles with geometric diameters less than 10 \( \mu \)m is unlikely because such small particles readily adhere to surfaces of large soil particles.

Processes for translocation and redistribution of environmental plutonium are both mechanical and chemical. Vertical transport in soil is slow compared to lateral redistribution by processes such as cultivation and erosion by wind and water currents. Other mobilization mechanisms, including biological
transport, depend on the solubility of the plutonium in water. In water, distribution constants, that is the fraction of the total Pu dissolved, are in the $10^{-4} - 10^{-9}$ range, showing that plutonium is an insoluble solid with a solubility similar to that of glass ($\text{SiO}_2$).

Chemical uptake by biological systems occurs via several pathways. The plutonium fraction transferred by root uptake of plants ranges from $10^{-3}$ to $10^{-5}$. Particle inhalation by grazing animals is of negligible concern compared to their gastrointestinal uptake. The fraction of ingested plutonium absorbed is approximately $10^{-4}$, and the combination of the plant uptake and animal ingestion from plant sources shows that the fraction of deposited Pu translocated to herbivores is $10^{-7}$ to $10^{-9}$. Behavior in marine and fresh water systems is similar; however, Pu concentrations in edible species (e.g., fish and crustaceans) in seawater vary from 30 to 3000 times that of edible species in fresh water.

The effects of plutonium on human health and longevity are the primary concern. Biologically, Pu is classified as a radiotoxin. The risk of cancer death is estimated to increase by 0.2% (2 in 1,000) for a person who breathes highly contaminated air (0.1 µg of respirable oxide per cubic meter) for one hour. Homogeneous dispersal of one kilogram of oxide in a typical municipal water supply would result in a Pu concentration of about 1 nanogram of Pu per liter. The increased risk of cancer death for a person who drinks two liters of that water per day for seventy years is estimated to be 0.01% (1 in 10,000).

### Relevant Studies

Although the mission of TA-55 does not include studies on environmental Pu, work being conducted under the Plutonium Repackaging Program is directly related to hazard assessments for incidents involving both facilities and weapons. Unlike Pu metal, PuO$_2$ is a powdered material with potential for environmental dispersal. Studies are underway to measure the size distributions for oxides from different sources and define the mass fractions of dispersible ($< 10 \, \mu\text{m}$ geometric diameter) and respirable ($< 3 \, \mu\text{m}$ geometric diameter) particles.

Results show that the dispersible and respirable fractions of the oxide vary by a factor of about $10^4$ depending on the method of preparation. A credible assessment of the dispersal hazard is possible only if the oxide source is considered.

### Human Effects of Environmental Plutonium

As with animals, incorporation of plutonium by humans also occurs primarily by inhalation and ingestion. Inhalation is of concern only in instances of accidental release where local concentrations are high for a short time. Studies of human populations give uptake fractions of $10^{-4}$ to $10^{-8}$ for ingested Pu.
Cessation of nuclear testing and the end of the Cold War caused the DOE weapons design laboratories to rethink their policies and practices for maintaining expertise in nuclear weapons science and for ensuring the integrity and safety of the increasingly smaller nuclear arsenal. In particular, weapons were originally intended for a stockpile life of approximately 25 years, but current knowledge and data indicate that the weapon life cycle may be extended beyond 25 years before the degradation of materials affects their performance.

Extending the stockpile life of existing nuclear weapons requires knowledge of the effects of aging on plutonium. In the past it was possible to remove a unit from the stockpile and test it in an underground explosion to measure any aging effects directly. Thus, much less knowledge of the specific materials and their influence on weapon performance was required. Without the advantage of underground weapons testing, we must now study the material itself.

Within the weapon pit component, clearly, it is the plutonium that causes aging-induced changes. The other components consist of relatively inert and otherwise well-protected materials. The materials-science-related phenomena that are likely to create changes in the plutonium can be categorized into three major areas: decay, equation-of-state, and high chemical reactivity.

Plutonium is radioactive (the 239 isotope has a half-life of approximately 24,000 years) and decays by emitting alpha radiation. Internally trapped alpha particles evolve into helium atoms, which can accumulate to about a thousand atomic parts per million over a 20- to 30-year time frame. Helium is known to cause embrittlement and swelling of metals such as stainless steel. The formation of such helium bubbles could affect the structural stability of the plutonium.

Another event that accompanies the ingrowth of helium during alpha decay is the injection of a uranium atom. Besides the possible chemical effects of the uranium atom on phase stability and physical properties, the recoil part of the nuclear decay process occurs at a high energy level, during which, it is conjectured, the uranium atom displaces many plutonium atoms before coming to rest. The defects thus produced may result in altering the chemical and physical stability of the plutonium.

Figure 2: Helium bubbles are shown in 20-year-old plutonium. Helium generation affects plutonium properties in weapon components.
Another measurable radiolytic process involves the decay of residual $^{241}\text{Pu}$, which results in the ingrowth of americium in the metal matrix. Americium may affect plutonium phase stability, but this phenomenon has not been studied conclusively.

Plutonium research efforts at Los Alamos have accomplished many noteworthy goals, such as determining many known plutonium binary phase diagrams, thorough study of the physical and mechanical properties of the stable metallurgical phases, and development of the “tailwind” and “trunk” alloys, now standards in the stockpile. In the middle to late 1980s, new techniques such as transmission electron microscopy and neutron scattering were applied to plutonium, resulting in detailed studies of the crystallography and structure of the $\delta\rightarrow\alpha$ martensitic phase transformation, the first observation of helium bubbles in aged plutonium (Figure 2), and the determination of Debye-Waller factors for both $\alpha$- and $\delta$-phase alloys. In the last few years small efforts have resulted in new technique breakthroughs, such as the advent of ultraviolet photoelectron spectroscopy, the laser-induced miniflyer technique (shock compression), and the extended x-ray absorption fine structure technique, which hold even further hope for understanding and predicting the behavior of plutonium under storage conditions. Such studies are important for thorough stockpile stewardship.

Several well-defined requirements within the new Stockpile Stewardship and Management Program necessitate renewed plutonium materials science activity. These requirements include recertification of existing weapons, a replacement-level pit manufacturing capability, and enhanced surveillance. Plutonium materials science research at Los Alamos now requires renewed commitment and funding to support enhanced stockpile surveillance, recertification of weapons, and replacement manufacturing.

Specific plutonium research topics at Los Alamos that are underway or proposed are divided into four major areas:

- Characterization of the effect of radiolytic helium on plutonium properties,
- Effect of aging on phase stability and density of plutonium,
- Surface physics and chemistry of plutonium metal, and
- Dynamic studies (shock compression) of plutonium and other weapons and materials.

Experiments will require close interaction by the major participating divisions within the Laboratory. We suggest that a committee chaired by a major funding program manager and a representative from each of the participating divisions coordinate this enhanced stockpile surveillance effort.

Figure 3. Computer simulation of plutonium casting. Such simulations are used before plutonium parts are cast to study the behavior of the material in the casting process and to avoid defects.
Division Director Discusses Plutonium Future Part 2

“and they shall beat their swords into plowshares, and their spears into pruning hooks: nation shall not lift up sword against nation, neither shall they learn war anymore.” Isaiah 2:4

Presently there is no international consensus on the disposition of excess plutonium released from weapons dismantlement. An approach that is being considered by most nuclear states, but not by the U.S. at this time, is utilizing plutonium as fuel to extract the available energy. In this context, weapons plutonium can serve as an initial step towards the recycling of plutonium for use in the civilian fuel cycle. There are no technical barriers to this option, but a myriad of timing, political, and fiscal barriers exist. Some of the world’s weapons materials are currently vulnerable to diversion, and because of the urgency to reduce the potential of nuclear threats, we can ill afford to wait for the political debate. Current U.S. policy is not to reprocess and recycle plutonium in commercial reactors, and the financial incentives to burn plutonium in nuclear power reactors are lacking in this, the world’s most energy-intensive nation.

The urgent issue is how to secure excess weapons plutonium against potential theft and diversion while the international debate on disposition policy continues. The National Academy of Sciences has stated that the excess plutonium in the world’s stockpile represents a clear and present danger to national security. So the question is: How can we preserve this potentially valuable resource for the future while dealing today’s realities? There is a logical appeal to the idea that the solution for dealing with excess plutonium from weapons has a parallel path to that for spent reactor fuel, and that the two paths converge at a decision point 50 years in the future.

The top-level tasks for the weapons plutonium project would be
1. dismantle weapons,
2. stabilize residues,
3. separate plutonium from weapons components and residues,
4. discard the low-level and nonnuclear wastes in permanent repositories,
5. convert the plutonium into inspectable forms of oxide or metal, and
6. store the plutonium in containers that can be certified and safeguarded for 50 or 100 years. Then let the political and economic debates rage and settle, and assuming the conclusion is the peaceful use of the nuclear fuel cycle,
7. convert the plutonium to mixed-oxide fuel,
8. recycle it in reactors, and eventually
9. reprocess and recycle plutonium in advanced reactor fuel cycles.
Technical solutions needed to complete this sequence have been developed as follows:

- disassembly, stabilization, and separation technologies for dismantled weapons and the 50-year legacy wastes are well established;
- disposal of nonnuclear or low-level nuclear waste is economically attractive and more environmentally acceptable than storing high-level radioactive wastes;
- the long-term stability of plutonium oxide and metal is well understood; and storage containers designed to last for 50 years have been fabricated and are in use.

Safeguarding the plutonium seems fairly simple because the amount of estimated excess weapons-grade plutonium metal could fit in two or three pickup trucks. (Of course the trucks would collapse, and the mass would be supercritical, but the image helps to visualize the magnitude of the problem.) One or two storage facilities containing 99.5 metric tons of separated plutonium could be readily safeguarded against theft and diversion for 50 years.

The actions for dealing with spent fuel are somewhat more complicated because of the profuse numbers and the dispersion of spent fuel assemblies around the nation and the globe. An additional 800 metric tons of reactor plutonium are contained— and still growing at about 50 tons per year—in spent nuclear reactor fuel. The spent nuclear fuel, along with about 90 metric tons of separated, reactor-grade plutonium, is presently stored in the 30 countries with civil nuclear power programs. Ironically, the intense radioactivity of spent fuel reduces the threat of its theft and diversion and therefore decreases the urgency of dealing with it. The parallel, top-level tasks for dealing with spent nuclear fuel might be

1. temporary storage in pools, followed by
2. retrievable dry storage in aboveground containers, thereby allowing time to debate the use of plutonium as a future energy source, and assuming the conclusion is the peaceful use of the nuclear fuel cycle,
3. reprocessing spent fuel,
4. discarding the fission product wastes in permanent repositories,
5. fabricating mixed-oxide fuel,
6. recycling the fuel in reactors, and
7. reprocessing and recycling plutonium in advanced reactors.

The energy content of the weapons plutonium in the U.S. has about the same energy content as 100,000,000 metric tons of oil; the energy content of spent fuel could increase the energy available from the once-through uranium cycle by nearly 100 times. This energy source could contribute to worldwide economic stability and reduce worldwide pollution from burning of fossil fuels. The barriers to achieving the vision of Isaiah with weapons-grade plutonium are significant but relatively simple: overcoming the aversion to separate, store, and use weapons-grade plutonium for peaceful uses, and reversing the restrictions on reprocessing and recycling reactor-grade plutonium.

Success depends on nations agreeing with nations on strict safeguarding and security of reactor-grade plutonium; I’m not optimistic, but I’m hopeful. In the meantime, the mission that we are facing is every bit as challenging, technically exciting, and important as the Manhattan Project. Whatever the political decisions and economic drivers; TA-55 will play a key role in developing new technologies for utilizing, managing, and ensuring the safety of the world’s plutonium.

Bruce Matthews
Does the Interaction of Plutonium Oxide with Water Pose a Potential Storage Hazard?

Recent world events have resulted in downsized nuclear arsenals and focused attention on additional ways of reducing the nuclear danger. Proper disposal of the surplus weapons-grade plutonium from dismantled weapons is necessary to prevent its diversion and reuse in weapons by proliferant states or terrorists. Most nations plan to use plutonium from both commercial reactors and weapons for nuclear power generation; the United States is considering various alternatives. Since selection and completion of a disposal option will probably take many years, surplus plutonium must be stored safely for an extended interim period.

DOE standards are established for storing surplus plutonium as metal (Pu) or as dioxide (PuO₂). After appropriate processing and certification, these materials are doubly confined in leak-tight stainless steel containers. According to popular belief, oxide is a stable material and the preferred form for storing plutonium. However, storage of oxide is more complicated than storage of metal. If hydrocarbons such as oils and plastics are present with the stored plutonium, whether metal or plutonium oxide, they undergo radiolytic decomposition by alpha particles from the radioactive decay of the plutonium, and this decomposition generates hydrogen gas. Whereas metal consumes the hydrogen by forming plutonium hydride, hydrogen produced in an oxide container pressurizes the vessel and may lead ultimately to rupture and the release of plutonium.

The Problem

Plutonium dioxide typically exists as a fine powder, and various hydrogen-containing species adsorb on its surface. Although oxide is processed by firing in air at 950°C to remove water, hydrocarbon, and other species before storage, water readily re-adsorbs when the oxide is exposed to room air during packaging operations. The fate of adsorbed water during storage is a concern.

Does residual water on the oxide pose a potential storage hazard? The answer to that question is a qualified “No.” If oxide is prepared, certified, and packaged according to procedures developed by NMT Division, the amount of residual water is far too small to cause problems. However, the situation would be different if oxide were to be packaged mistakenly without being fired.

Two processes by which adsorbed water might generate pressure in oxide-containing storage vessels are being investigated by members of the Applied Weapons R&D Team in NMT-5. As described by the following reactions, these processes are (1) radiolytic decomposition of adsorbed water into oxygen and hydrogen and (2) chemical reaction of dioxide and water to form a higher-composition oxide (PuO₂ₓₐ) and hydrogen:

\[
\begin{align*}
\text{a-particle} & \\
\text{H}_2\text{O (adsorbed)} & \rightarrow \text{H}_2 (g) + 1/2 \text{O}_2 (g). & (1) \\
\text{PuO}_2 (s) + x \text{H}_2\text{O (adsorbed)} & \rightarrow \text{PuO}_{2+x} (s) + x \text{H}_2 (g). & (2)
\end{align*}
\]

Figure 4. This failed storage container (left) containing Pu metal was packaged in air containing some moisture. Whereas one end bulged, the weld on the other end (right) failed and ruptured. The drastic failure occurred after just a few days.

The work presented here implies that water is a better oxidizing agent than oxygen, which is difficult to prove. The question also remains whether the extra oxygen in PuO₂ₓₐ is actually adsorbed on the surface or incorporated into the lattice.
published results showing that a PuO$_{2+x}$ phase forms on the dioxide surface in water vapor at 250˚C to 300˚C. The product is a mixed-valance oxide of Pu (IV) and Pu (VI) with $x \leq .3$.

A number of questions remain to be answered:
- Does any significant reaction occur at room temperature?
- Does some other unanticipated reaction occur?
- How fast are these reactions?
- Are their rates fast enough to present a potential storage problem?
- Do O$_2$ and H$_2$ combine to form water?
- Is the recombination rate faster than the rate of radiolytic decomposition?

Experimental Approach

With so many questions to be answered, a large research effort might be anticipated. However, essential questions relevant to the storage issue are readily addressed by simple pressure-volume-temperature (PVT) experiments. After reactants are sealed in a vessel of known volume, the temperature and pressure are monitored over time. Reaction rates are defined by changes in pressure with time. The reaction is identified by analysis of the gaseous products.

Two PVT experiments were conducted using PuO$_2$ prepared by reacting high-purity Pu with oxygen. In one test the oxide-containing reaction vessel was evacuated and backfilled to the saturation pressure of liquid D$_2$O at room temperature. In the other test the vessel was backfilled with approximately 125 torr of a mixture with D$_2$ and O$_2$ in a 2:1 ratio.

Analytical results for the test with D$_2$O are the key to defining chemical behavior. Radiolytic decomposition, Reaction 1, is the important reaction if D$_2$ and O$_2$ appear in a 2:1 ratio. Likewise, the formation of pure D$_2$ shows that water reacts according to Reaction 2. Occurrence of both reactions produces a mixture with a hydrogen:oxygen ratio greater than 2.

The importance of radiolytic decomposition is most easily shown by comparing the pressure changes for the two tests. Radiolysis cannot result in pressurization of an oxide storage container if the oxygen and hydrogen recombine to form water (reverse of Reaction 1) at a faster rate than that of the forward reaction.

Results and Conclusions

Results of the test with D$_2$O show that adsorbed water reacts chemically with PuO$_2$ to form D$_2$, according to Reaction 2. The pressure increases at a constant rate over time, and hydrogen is the only gaseous product. At the measured rate a high hydrogen pressure can be produced in a few years in a typical storage container.

An explanation for the apparent absence of radiolytic decomposition is suggested by kinetic results for the D$_2$+O$_2$ mixture. As shown in Figure 5, the pressure in the mixture dropped rapidly during the first few days and gradually slowed to an almost constant decrease that has continued for more than a year. The rate at which hydrogen and oxygen combine on the catalytic surface of PuO$_2$ is so fast that radiolytic decomposition is not observed. Occurrence of Reaction 1 is not a concern for oxide storage. The D$_2$:O$_2$ ratio of the gas mixture is progressively increasing over time because the D$_2$O product is reacting with the oxide as described in Reaction 2.

The results demonstrate that excessive pressurization of a storage container might occur if the oxide were improperly fired or if unfired oxide were mistakenly packaged. Although all questions presented above have been answered, additional studies are being conducted to determine how the rate of Reaction 2 depends on temperature and on the concentration of water adsorbed on the oxide.

Spinoff

The importance of these findings extends far beyond their relevance to storage safety. Further study of the formation of PuO$_{2+x}$ might help to explain why environmental plutonium appears as high-oxidation-state ions in solution and why high-fired oxide tends to be insoluble. Results of the oxygen-hydrogen combination study have already been used to explain why atmospheric corrosion of plutonium metal is accelerated by moisture.

Journal Publications


Invited Talks


Conference Presentations


The following papers were presented at JOWOG 22 Conference on Actinide Stabilization, Packaging and Storage, Los Alamos National Laboratory, May 21-22, 1996: J. M. Haschke, “Discussion of Known Container Failure Mechanisms,” “Plutonium Metal, Oxide and Residue Stabilization Parameters,” “Pressurization and Condensation in Long-Term Storage Containers,” and “Recent Findings.”

Reports


The Science and Technology Panel of the University of California President’s Council on the National Laboratories visited Los Alamos on April 19 to be briefed on programmatic activities of several divisions. For NMT, Division Director Bruce Matthews gave an hour-long presentation on NMT’s responses to the observations and concerns raised by the DRC in its most recent report, several new programmatic initiatives undertaken by the division, the funding outlook for both science and technology, and facility and infrastructure support.

LDRD News
A Laboratory Directed Research and Development (LDRD) proposal by Larry Avens (NMT-6) and a number of co-principle investigators has been selected for funding at one million dollars for five years. The title of this winning proposal is “Actinide Molecular Science,” and it proposes a fundamental investigation into a broad range of actinide science topics.

As of May 20, the last day for the 1997 LDRD proposals, NMT technical staff members submitted a record number of individual projects and program development proposals. Ed Heighway, LDRD Office Leader, sends a message that he is delighted to see NMT is playing an improved and significant role in the Laboratory’s LDRD program.
Division Director Bruce Matthews presented a colloquium titled “The Plutonium Legacy” at the University of California (UC), Berkeley, on April 15. The audience came from both the Nuclear Engineering and Materials Science and Mineral Engineering Departments. Several faculty members and students expressed strong interest in continued dialogue and potential collaborative work with Los Alamos.

Bruce Matthews was elected to the rank of Fellows of the American Nuclear Society. The citation reads, “For his unique contributions in nuclear fuels technology development (fabrication, testing, and demonstration) and being an ardent proponent of safe, beneficial uses of nuclear technologies for the nation and the world.”

Paul Cunningham served as Science Counsel in Vic Reis’ Washington office during March, April, and May. Reis is the Assistant Secretary for Defense Programs in the Department of Energy (DOE). One aspect of Cunningham’s assignment was to arrange a “Plutonium Workshop” for Defense Programs contractors and DOE personnel.

Dana Christensen gave colloquia at UC Davis (May 20), New Mexico State University (NMSU) (April 2), and New Mexico Institute of Mining and Technology (April 3). He informed his audiences on the state of current nuclear materials and nuclear weapon activities. He also discussed potential collaborations with faculty and students at all three campuses, including summer and sabbatical assignments and support for campus projects.

Consultant Gerd Rosenblatt spent two days with us on March 21 and 22, and two days on May 13 and 14. Rosenblatt is the former Deputy Director of Lawrence Berkeley National Laboratory (retired) and was Division Leader of the Los Alamos Chemistry Division. He will advise the NMT Division Director and the Nuclear Materials and Stockpile Management Program Director on science and technology issues, facilitate university interactions, and help in recruiting scientists and students.

NMT has a new Division Review Committee member. Todd R. LaPorte is Professor of Political Science and formerly Associate Director of the Institute of Government Studies at UC, Berkeley. He teaches and publishes in the areas of public administration, organization theory, and technology and politics, with particular emphasis on the decision-making dynamics of large, complex, technologically intensive (and hazardous) organizations. Sound familiar to you at TA-55? We are very pleased that Professor LaPorte has joined us as a member of the NMT External Advisory Team. LaPorte’s first visit is scheduled July 11 and 12.

Keith W. Fife (NMT-2) submitted his Ph.D. dissertation in chemical engineering to NMSU’s Graduate School. Fife did his graduate work while maintaining a full-time career at TA-55. The dissertation is entitled “A Kinetic Study of Plutonium Dioxide Dissolution in Hydrochloric Acid Using Iron (II) as an Electron Transfer Catalyst.” Congratulations, Keith, for your hard work and for the successful completion of your Ph.D. program.